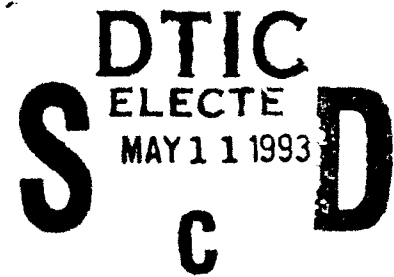


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APPLICATIONS OF TRANSITION METAL COMPOUNDS IN THE PREPARATION OF
USEFUL SILICON-CONTAINING CERAMICS

by

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Applications of Transition Metal Compounds in the Preparation of Useful Silicon-Containing Ceramics

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There have been many studies of the reactions of organosilicon compounds with diverse transition metal complexes [1]. The original impetus for this research activity was given by the discoveries that heterogeneous platinum and palladium catalysts [2,3] and chloroplatinic acid [3] were effective hydrosilylation catalysts. In the years that followed, many other transition metal complexes have been found to catalyze the addition of silicon hydrides to organic multiple bonds. Also, transition metal complexes have been found to catalyze other reactions of organosilicon compounds, such as the insertion of acetylenes and other unsaturated organic compounds into reactive Si-Si bonds [5] and reactions of the Si-C bonds of strained cyclic organosilicon compounds [6]. A different focus on silicon-transition metal chemistry was found in Aylett's preparation of H_3Si -transition metal compounds [7]. These were found to be effective precursors for transition metal silicides by chemical vapor deposition. This potentially useful application in materials processing led to further work by others on the synthesis of transition metal complexes containing metal-silicon bonds.

More recently, it was the seminal work of Aitken, Harrod and Samuel which showed that Group IV metallocene compounds catalyzed the dehydrogenative coupling of primary silanes, $RSiH_3$, to give polysilanes of relatively low molecular weight, $[RSiH]_n$ [8], that attracted many others into the silicon/transition metal chemistry field [9].

In our research at MIT we have found transition metal chemistry a very useful aid in the preparation of silicon-containing ceramics by the polymer pyrolysis procedure.

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One of the silicon-containing preceramic polymers that we prepared is poly(methylsilane). It was discovered by T.G. Wood in our laboratories [10] and, independently, by Brown-Wensley and Sinclair at the 3M Company [11], that the action of an excess of metallic sodium on methylchlorosilane, $\text{CH}_3\text{SiHCl}_2$, results in complete dechlorination and usually partial dehydrogenation to give polysilanes of type $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y(\text{CH}_3\text{SiH}_2)_z]_n$. The CH_3SiH_2 end groups are detectable by ^{29}Si NMR (DEPT). For simplicity's sake, we write the polysilane as $[(\text{CH}_3\text{SiH})_x(\text{CH}_3\text{Si})_y]_n$, where $x + y = 1$ and x and y are derived from the integrated ^1H NMR spectrum. The CH_3SiH_2 end groups could result from a disproportionation reaction, but their provenance is unknown at this time. When the $\text{CH}_3\text{SiHCl}_2/\text{Na}$ reaction is carried out in 7 : 1 (v/v) hexane/tetrahydrofuran (THF), very little Si-H functionality is lost and $x \sim 0.75 - 0.98$. When, on the other hand, the reaction is carried out in THF alone, there is substantial loss of Si-H functionality and $x \sim 0.4$. Those poly(methylsilanes) where $x \sim 0.75 - 0.98$ are liquids of relatively low molecular weight ($n \sim 14-16$). Since their extent of crosslinking is very low, the ceramic residue yield obtained in their pyrolysis in argon is low (15 - 25%). A substantial fraction of the methyl groups is lost as CH_4 in the pyrolysis. As a result, the pyrolysis residue contains around 24% by weight of elemental silicon as well as the expected $\beta\text{-SiC}$. The poly(methylsilane) that is produced in the reaction carried out in THF is a soluble solid and is more highly crosslinked. Consequently, its pyrolysis gives a 60% ceramic residue yield. However, here also methyl group loss is substantial and the ceramic residue again contains about 25% elemental silicon.

These problems, low ceramic yield and formation of substantial amounts of elemental silicon in the pyrolysis, can be dealt with in a number of ways. Transition metal-catalyzed cross-linking has been found to be particularly effective [12].

In view of Harrod's findings that $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}(\text{CH}_3)_2$ ($\text{M} = \text{Ti}, \text{Zr}$) compounds are effective catalysts for the dehydrogenative coupling of mono- and diorganosilanes, we studied the action of these and related complexes on the liquid poly(methylsilane) obtained by sodium condensation of $\text{CH}_3\text{SiHCl}_2$. The compounds $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrH}_2]_n$,

$(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrHCl}$, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)_2$ and $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$ were found to be effective catalysts for the crosslinking of poly(methylsilane). Products that were still soluble but that on pyrolysis gave ceramic residue yields in the range 70-85% were obtained. The catalysts, used in 0.5 - 1.5 mol % quantity, could be activated by UV irradiation (methyl compounds only) or thermally. An added, unexpected benefit of using these catalysts was that the pyrolysis residue was near-stoichiometric silicon carbide. Thus in the case of the $[(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrH}_2]_n$ catalyst, the residue, by elemental analysis, had the nominal composition, by weight, 98% SiC, 1.6% ZrC and 0.4% Si. X-ray powder diffraction of the residue showed lines due to β -SiC and none due to elemental silicon. Integration of the proton NMR spectra of the poly(methylsilane) before and after treatment with the organozirconium or -titanium catalyst showed that there had been a significant loss of Si-H functionality. Thus dehydrogenative coupling very likely had taken place. The ^{29}Si NMR spectrum of the crosslinked poly(methylsilane) showed that the CH_3SiH_2 moieties (which could be expected to be more reactive than the internal CH_3SiH groups) had almost disappeared. The catalyst residues, being nonvolatile, remained in the polymer and thus some small amounts of TiC or ZrC ended up in the ceramic obtained on pyrolysis of the crosslinked poly(methylsilane). At this time it is not known whether or not the transition metal moieties are chemically bound to the poly(methylsilane).

In view of current interest in composites containing two or more ceramics, e.g., SiC/TiC [13], we have extended this work to include stoichiometric reactions of the liquid poly(methylsilane) with $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}(\text{CH}_3)_2$ ($\text{M} = \text{Ti, Zr, Hf}$) compounds [14]. The UV irradiation of mixtures of these reactants in hexane under argon resulted in formation of THF- and toluene-soluble brown to black, air-sensitive solids that still contained η^5 -cyclopentadienyl groups. Their pyrolysis, in argon to 1500 °C, gave ceramic residues in high yield. X-ray diffraction established the presence of β -SiC as well as of the respective MC and elemental analysis indicated that substantial amounts of free carbon were present. Selected results are given in Table I. The excess free carbon was undesirable and could be dealt with in two ways. In the first, the ceramic product, was heated to ~1000 °C in a

Table I. Ceramics Obtained in the Pyrolysis of the Methylpolysilane/ $(\eta^5\text{-C}_5\text{H}_5)_2\text{MMe}_2$ Reaction Product Polymers to 1500° C in a Stream of Argon

| | SiH : Metal Ratio | Ceramic Yield | Relative molar amount of phase (% by weight of phase) | | |
|--------|-------------------|---------------|--|-----------------|-----------------|
| | | | MC | SiC | C |
| M = Ti | 1.00 : 1.05 | 78% | 1.00 (28.9%) | 1.61 (31.2%) | 6.85 (39.9%) |
| M = Zr | 1.00 : 0.49 | 84% | 1.00 (29.3%) | 3.69 (42.0%) | 8.43 (28.7%) |
| M = Hf | 1.00 : 0.32 | 67% | 1.00 (34.8%) | 6.24 (45.7%) | 8.90 (19.5%) |

stream of ammonia. This served to react away the free carbon (as HCN and H_2 [15]) and to convert the ZrC to zirconium nitride. Thus a SiC/ZrN composite had resulted. Alternatively, enough of a metal powder was added to poly(methylsilane)/ $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}(\text{CH}_3)_2$ reaction product to react with the expected free carbon at high temperature [14]. Thus when in one experiment an intimate mixture of the poly(methylsilane)/ $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{CH}_3)_2$ reaction product and titanium powder was heated to 1500 °C in argon, a ceramic product that X-ray diffraction showed to contain β -SiC and TiC was obtained. Elemental analysis established a nominal composition of 64.5% TiC, 35.0% SiC and 0.5% C (by weight). A ternary composite could be prepared when, for instance, $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CH}_3)_2$ was used and the added metal powder was Ti. The pyrolysis of intimate mixtures of silicon-containing preceramic powders with transition metal powders has been used to generate ceramic phases other than those obtained when the polymer is pyrolyzed alone [16]. Tables II and III give selected results for such pyrolyses of the $[(\text{CH}_3\text{Si}(\text{H})\text{NH})_a(\text{CH}_3\text{SiN})_b]_n$ polysilazane [17] with transition metal powders in argon and in ammonia; Table IV, selected results of the pyrolysis of the Nicalon polycarbosilane with transition metal powders in argon. It is seen that this procedure provides a useful route to MC/SiC composites, to transition metal silicides and, in cases where the metal nitride is very stable, to SiC/MN composites.

Table II. Ceramic Products from Metal Powder-Polysilazane Composites Pyrolyzed to 1500° C Under a Flow of Argon.

| Metal | M : Si | Ceramic yield (%) | XRD results |
|-------|---------|-------------------|--|
| Ti | 1.2 : 1 | 72 | TiN + SiC |
| Zr | 1.3 : 1 | 82 | ZrN + SiC |
| V | 1 : 1 | 54 | V ₅ Si ₃ + SiC |
| Nb | 1 : 1 | 80 | NbC + NbSi ₂ |
| Mo | 1 : 2 | 73 | MoSi ₂ + Mo ₅ Si ₃ |
| Mo | 1 : 1 | 80 | Mo ₅ Si ₃ |
| W | 1 : 1 | 87 | WC + WSi ₂ + W ₅ Si ₃ + SiC |
| W | 5 : 3 | 93 | WC + W ₅ Si ₃ |

Table III. Ceramic Products from Metal Powder-Polysilazane Composites Pyrolyzed at 800° C for 4h Under Ammonia Flow, then at 1500° C Under a Flow of Argon.

| Metal | M : Si | Ceramic yield (%) | XRD results |
|-------|--------|-------------------|---|
| V | 1 : 1 | 49 | V ₂ N + V ₅ Si ₃ |
| Mo | 1 : 1 | 73 | Mo ₅ Si ₃ |
| W | 1 : 2 | 76 | W ₅ Si ₃ + WSi ₂ |
| W | 5 : 3 | 89 | W ₅ Si ₃ * |

* Anal.: W, 93.32; Si, 4.42; C, N, <5.

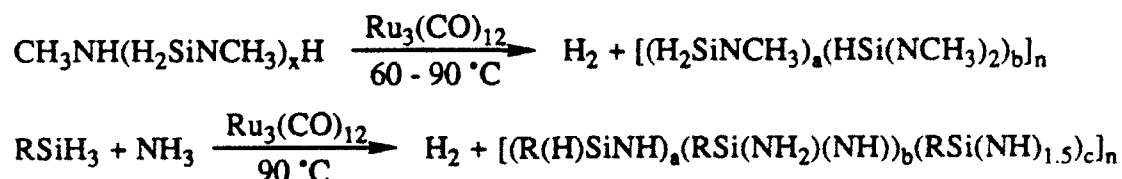
Table IV. Ceramic Products from Metal Powder-Nicalon PCS Composites Pyrolyzed to 1500° C Under a Flow of Argon.

| Metal | M : Si | Ceramic yield (%) | XRD results |
|-------|--------|-------------------|---|
| Mo | 1 : 1 | 91 | α-Mo ₂ C + Mo ₅ Si ₃ + SiC |
| W | 1 : 2 | 85 | WC + WSi ₂ + SiC * |
| Ti | 1 : 1 | 80 | TiC + SiC |
| Zr | 1 : 1 | 87 | ZrC + SiC |
| V | 1 : 1 | 79 | V ₈ C ₇ + SiC |
| Nb | 1 : 1 | 85 | NbC + SiC |
| Ta | 1 : 1 | 83 | TaC + SiC |

* Anal.: W, 68.73; Si, 16.77; C, 10.80 (equiv. to ~ 0.38 WC, 0.59 SiC, 0.03 WSi₂)

Other organosilicon polymer precursors for ceramics have either been prepared or improved by means of transition metal complex-catalyzed chemistry. For instance, the Nicalon silicon carbide-based ceramic fibers are fabricated from a polycarbosilane that is produced by thermal rearrangement of poly(dimethylsilylene) [18]. The $\text{CH}_3(\text{H})\text{SiCH}_2$ group is the major constituent of this polycarbosilane. Pyrolysis of the uncured Nicalon polycarbosilane typically gives ceramic residue yields of 55-60%. We found that this polymer may be further crosslinked to give soluble products by treatment with small quantities (0.25 - 1.5 mol%) of a metal carbonyl, using either UV irradiation or thermal activation [19]. $\text{Co}_2(\text{CO})_8$, $\text{Co}_4(\text{CO})_{12}$ are particularly effective. This approach was suggested by the known stoichiometric reactions of molecular organosilicon hydrides with transition metal carbonyls to give products containing transition metal-silicon bonds [20]. Pyrolysis of these crosslinked polymers resulted in ceramic residue yields in the 80-90% range.

Polysilazanes that can serve as precursors for silicon carbonitride have been prepared using a $\text{Ru}_3(\text{CO})_{12}$ -catalyzed Si-H/N-H dehydrogenative coupling process by workers at SRI [21]. Thus the ammonolysis product of $\text{CH}_3\text{SiHCl}_2$, whose composition approximates $[\text{CH}_3\text{Si}(\text{H})\text{NH}]_n$, could be crosslinked by heating at 40 °C with a catalytic quantity of $\text{Ru}_3(\text{CO})_{12}$. Other polysilazanes were prepared by this procedure:



This brief review has shown that the transition metals and their compounds can play a very useful role in ceramics-directed silicon chemistry. Transition metal complexes find important applications as catalysts as well as stoichiometric reactants, and the metals themselves have found more direct application in the synthesis of silicon-containing ceramics and ceramic composites.

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